

**THE DURATION OF CHEMICAL WEATHERING OF GUSEV CRATER'S WISHSTONE-WATCHTOWER SEQUENCE.** B. Sutter<sup>1</sup>, D.W. Ming<sup>2</sup>, and D.C. Golden<sup>3</sup>, <sup>1</sup>Jacobs/ESCG, Houston TX, 77058, brad.sutter-2@nasa.gov. <sup>2</sup>NASA Johnson Space Center, Houston, TX 77058. <sup>3</sup>ESCG/Hamilton Sundstrand, Houston, TX 77058.

**Introduction:** Mineralogical abundance of primary minerals versus secondary minerals, chemical mixing relationships, and elemental ratios have been used to assess the degree of aqueous alteration at Gusev Crater and Meridiani Planum [e.g., 1, 2, 3, 4, 5]. However, limited work has used Ti-normalized mass-balance analysis chemical data to quantify gains and losses of elements from altered materials as well as estimate the duration of aqueous alteration on Mars [6, 7]. The Ti-normalized mass-balance approach accounts for volumetric changes associated with geochemical alteration. If volumetric changes are not considered, observed geochemical trends based on un-normalized data have the potential to be misleading. Assessing gains and losses from altered materials can indicate the geochemistry of fluids involved in the alteration. Furthermore, elemental losses can be combined with dissolution rates to estimate the duration of chemical weathering. Knowledge of the duration of aqueous alteration will provide insight into the climate history of Mars as well as indicate the potential for microbial habitability. The Wishstone-Watchtower materials in Gusev Crater are suitable candidates for Ti-normalized mass-balance analysis because mixing relationships of these two materials indicate that Watchtower materials may be derived from Wishstone-like materials [8]. The objectives of this work are to (1) employ Ti-normalized mass-balance to assess gains and losses from the Wishstone-Watchtower sequence and (2) to combine losses with laboratory dissolution rates to estimate alteration times of the Watchtower material.

**Methods:** The mass-balance equation was used to calculate elemental gains and losses (equation 1) [9,10]. The mass transport ( $\tau_{jw}$ ) of an element (j) in the weathered soil or altered rock (w) compared to its parent material (p) is calculated relative to an immobile element (i), where C is concentration of the respective elements:

$$\tau_{jw} = (C_{jw}/C_{iw} // C_{jp}/C_{ip}) - 1 \quad (1)$$

The gain or loss of mobile elements is determined by referencing the mobile element to an immobile element (e.g., Ti, Zr, Nb). When  $\tau_{jw}$  is 0, the element is immobile; negative values indicate the element was removed from the weathered material, and positive values indicate the element was added from a source other than the parent material. For example, when  $\tau_{jw} = -0.30$ , 30% of that element has been lost from wea-

thered material relative to that element's starting concentration in the parent material.

Na loss was detected and determined to be derived from feldspar dissolution. Subsequently the remaining fraction (f) of feldspar is determined by

$$f = [(mM_{start} - mM_{end})/mM_{start}] \quad (2)$$

$mM_{start}$  and  $mM_{end}$  refer to literature starting concentration of feldspar and calculated ending mineral concentration, respectively. If a starting particle size is assumed for a particular mineral then the fraction of the mineral that remains and its new particle size can be estimated by

$$\sqrt[3]{f \cdot r_{start}^3} = r_{end} \quad (3)$$

where  $r_{start}$  is the starting radius while  $r_{end}$  is the radius after the mineral has been dissolved.

The time for mineral dissolution is then calculated using the following equation [11]:

$$time = \frac{r_{end} - r_{start}}{-k \cdot V_m} \quad (4)$$

Where  $k$  is the literature rate constant and  $V_m$  is the molar volume of the mineral. For this work the rate constant is determined as a function of pH by [12]

$$\text{Log } k_{25C} = 9.5(\text{pH})0.5 + 11.8 + 9.9(\text{pOH})0.3 \quad (5)$$

The duration of dissolution can therefore be calculated as a function of pH and starting particle size.

The RATED Wishstone and Watchtower chemical data [13] were used to calculate gains and losses and to determine duration of chemical weathering.

**Results/Discussion:** Sodium is the primary element that was lost in the aqueous alteration of Wishstone to Watchtower materials (Table 1). Small losses/gains of Al, Ca, and P suggest that these elements are relatively immobile. Gains in Si, Fe, Mn, and Ni are indicated. Larger gains were determined for K, Mg, Zn, S, Cl and Br that mostly agree with the hypothesis that fluids enriched in Mg, Zn, S, and Cl were involved in altering Wishstone material to Watchtower material [8].

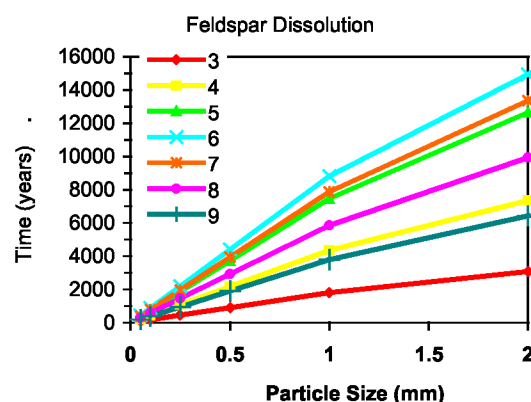
The moles of Mg, Fe, Si added to the Watchtower material indicates that the ratio of Mg and Fe to Si is 2.37. While this is not a perfect 2:1 ratio, this is close to the molar ratio of Mg and Fe to Si in olivine  $[(\text{Mg,Fe})_2\text{SiO}_4]$ .

**Table 1. Mass transport  $\tau_{jw}$  results for Watchtower-Joker-RAT relative to parent material Wishstone-Chisel-RAT.**

Element	$\tau_{jw}$	$\tau_{jw}$ error	mMoles/100g Gain/loss
Na <sub>2</sub> O	-0.372	0.042	-29.9
Al <sub>2</sub> O <sub>3</sub>	-0.039	0.002	-5.7
P <sub>2</sub> O <sub>5</sub>	0.016	0.001	0.59
CaO	-0.019	0.001	-3.1
SiO <sub>2</sub>	0.134	0.007	98.0
MnO	0.172	0.014	0.53
Ni	0.172	0.140	0.02
FeO	0.334	0.018	53.9
K <sub>2</sub> O	0.521	0.075	3.5
MgO	1.604	0.094	180.5
SO <sub>3</sub>	0.827	0.050	22.8
Cl	1.679	0.109	16.8
Zn	1.564	0.355	0.15
Br	12.371	9.069	0.34

This result suggests fluids involved in aqueous alteration of Wishstone to Watchtower may have derived Mg and Fe and Si from olivine dissolution. The ratio of Mg:Fe yields an olivine composition of (Mg<sub>1.5</sub>,Fe<sub>0.5</sub>)SiO<sub>4</sub>. The excess Fe and Mg could be derived by incongruent dissolution of olivine where Fe and Mg are preferentially released relative to Si. Another possibility is that some Si is lost from feldspar as indicated by the negative  $\tau_{jw}$  for Na. The overall positive Si  $\tau_{jw}$  is a summation of some Si loss from feldspar coupled with Si addition from an outside olivine source.

The calculated Na loss indicated that Wishstone parent material lost feldspar in the formation of the Watchtower material. The feldspar loss was used to calculate duration of aqueous alteration as function of pH and particle size (Fig. 1). If the pH is assumed to be 4 [8] in this system then Wishstone particles of 1 mm and 0.05 mm weathered over a period of 4300 and 217 years, respectively. However, laboratory rates used in these calculations can be 2 to 5 times faster than field rates [14] which can increase the time of aqueous alteration to as high as 45Kyr. Calculated aqueous alteration times are minimum times because laboratory rates are measured under high water to rock ratios, low ionic strength, and do not consider the formation of surface precipitates. Field conditions have low water:rock ratios, higher ionic strengths, and surface precipitates that inhibit mineral dissolution and thus decrease dissolution rates. The addition of Si from proposed olivine dissolution would also contribute to slowing the dissolution of feldspar as well.



**Fig. 1. Wishstone-Watchtower oligoclase dissolution times (y) as a function of particle size and pH.**

**Conclusions:** Titanium-normalized mass-balance results indicated that Na loss from feldspar dissolution occurred during the aqueous alteration of Wishstone to Watchtower materials. Minor gains in Fe, Mg, and Si suggested inputs from olivine dissolution from outside the Wishstone-Watchtower system. Alteration fluids also contained moderate levels of S and Cl. The amount of feldspar dissolution was derived from Na loss which was coupled with feldspar dissolution rates to estimate time of dissolution. Dissolution times of 217 to 4300 years were calculated and represent minimum times of dissolution. This work demonstrates the value of combining Ti-normalized mass-balance with laboratory dissolution rates in assessing duration of aqueous activity on Mars. Results from this work will serve as the foundation for developing more sophisticated kinetic dissolution calculations that will provide improved estimates of aqueous alteration times on Mars.

**References:** [1] Morris, R.V. et al., (2009) *JGR*, *Accepted*. [2] Ming, D.W. et al., (2008) *JGR*, 2008JE003195. [3] Hurowitz, J et al. (2006) *JGR*, 111, 2006JE002795. [4] Schmidt, M.E. et al., (2008) *JGR*, 113, 2007JE003027. [5] Yen, A. et al., (2008), *JGR*, 113 2007JE0029791979. [6] Hausrath et al., (2008), *Geology*, 36, 67. [7] Amundson et al. (2008) *Geochim Cos. Acta* 72, 3845. [8] Hurowitz et al., (2006) *JGR*, 111, 2006JE002795. [9] Nesbitt, H.W. (1979), *Nature*, 279, 206. [10] Chadwick, O.A. et al., (1990) *Geomorph.*, 3, 369. [11] Lasaga, A.C. (1984), *JGR*, 89, 4009. [12] Blum, A.E. & Stillings, L.L., (1995), *Rev. Min.* 31, 291. [13] Gellert, R. et al. (2006) *JGR*, 111, 2005JE002555. [14] White, A.F. and Brantly, S.L. (2003) *Chem. Geol* 202, 279.